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Note

A new dimeric coumarin from *Boenninghausenia albiflora* Reichb and Meissner (Rutaceae)

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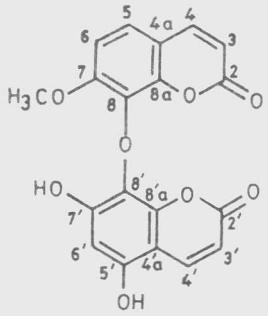
A new dimeric coumarin, Boennin, has been isolated from *Boenninghausenia albiflora* Reichb & Meissner. The structure of the compound as 1 has been established from spectral and correlation studies. The occurrence of two other minor coumarins, gravelliferone and luvangetin, has also been observed for the first time from this plant.

Earlier studies on the plant *Boenninghausenia albiflora* resulted in the isolation of eight coumarins[1-3]. The present communication concerns the structure elucidation of a new dimeric coumarin, Boennin (**1**). This is the first report of the occurrence of gravelliferone (**2**)[4] and luvangetin (**3**)[5] in *B.albiflora*.

Boennin (**1**), $C_{19}H_{12}O_8$ (M^+ 368), mp 239 °C (EtOH), exhibited UV absorption maxima at 352, 345, 327, 264, 255 and 214 nm (log ε 4.23, 4.23, 4.22, 3.84, 3.83 and 4.45 respectively) which shifted in alkali to 302, 239 and 227 nm (log ε 3.74, 4.24 and 4.25 respectively), characteristic of a phenolic coumarin. The presence of a hydroxyl function (3340 cm^{-1}), α,β-unsaturated δ-lactone moiety (1710, 1610 cm^{-1}), and aromatic nucleus (1495, 1450 cm^{-1}) could be ascertained from its IR spectrum. The 300 MHz ^1H NMR spectrum of



Boennin

boennin substantiated the presence of two coumarin nuclei. The C-4 and C-4′ protons appeared at δ 7.94 and 7.97 as one-proton doublet each (J = 9.0 Hz) and the C-3 and C-3′ protons at δ 6.15 and 6.29 as one-proton double t each (J = 9.0 Hz). The aromatic protons at C-5 and C-6 resonated as doublets at δ 7.52 and 6.91 (1H, d, J = 9.0 Hz each) while the C-6′ proton appeared as a singlet at δ 7.15, the C_7-OCH_3 at δ 3.74 (3H, s) and two phenolic -OH groups as a singlet at δ 7.50. The absence of C-8 and C-8′ protons indicated that the two coumarin units must be joined at this point. The presence of the ether linkage could be confirmed from the 75.5 MHz ^{13}C NMR spectrum. The C-8 and C-8′ values underwent downfield shift to 135.7 ppm. Negative ferric chloride test confirmed that the two phenolic groups were *meta* to each other. The structure of the product was established from its 75.5 MHz ^{13}C NMR data (Table I) and by correlation with jayantinin[1] (**4**).

Experimental Section

General. The plant material was collected from Chaubattia area of Ranikhet, District Almora, U P, India, during the month of October, and was identified by Shri R N Tewari and Shri S C Pant of IIADR, CCRAS, Tarikhet, Ranikhet.

General. A voucher specimen has been deposited at the Department of Pure Chemistry, University College of Science, University of Calcutta, India. Melting points were recorded using an electrically heated metal-bath and are uncorrected. UV spectra

Table I — ^{13}C NMR spectral data of Boennin in DMSO-d_6

Carbon No.	Chemical Shift (δ, ppm)	Nature of carbon in APT spectra
C-2	160.6	sp^2 quarternary
C-2′	160.3	sp^2 quarternary
C-3	113.8	sp^2 secondary
C-3′	113.3	sp^2 secondary
C-4	114.1	sp^2 secondary
C-4′	143.9	sp^2 secondary
C-4a	111.9	sp^2 quarternary
C-4′a	111.4	sp^2 quarternary
C-5	129.8	sp^2 secondary
C-5′	150.3	sp^2 quarternary
C-6	103.9	sp^2 secondary
C-6′	120.7	sp^2 secondary
C-8, C-8′	135.7	sp^2 quarternary
C-8a	155.3	sp^2 quarternary
C-8′a	154.9	sp^2 quarternary
C-7	159.9	sp^2 quarternary
C-7′	159.6	sp^2 quarternary
$-OCH_3$	56.1	sp^3 methoxyl

(in 95% aldehyde free ethanol) were recorded on a Hitachi 2000 spectrometer, IR spectrum on a Perkin-Elmer 782 spectrophotometer, NMR spectra on a Bruker AM-300 spectrometer and mass spectrum on a Jeol D-300 mass spectrometer. Silica gel (BDH, 60-100 mesh) and silica gel G (Merck, 350 mesh) were used for CC and TLC, respectively. Analytical samples were dried *in vacuo* over P_2O_5 for 24 hr.

Extraction. The air-dried plant material (root, 6.5 kg) was crushed and extracted with ethanol at room temperature for 30 days. The concentrated crude residue was chromatographed over silica gel and the column eluted with solvents of increasing polarity.

Isolation of Boennin 1. Boennin was obtained from the ethyl acetate eluate, and crystallised from ethanol (yield 0.0031%), m.p. 239 °C (EtOH), R_f 0.6 (benzene-ethyl acetate, 1:1); UV(EtOH) (nm): 352, 345, 327, 264, 255 and 224 nm (log ε 4.23, 4.23, 4.22, 3.84, 3.83 and 4.45); UV(EtOH + alkali): 302, 239, 227 nm (log ε 3.74, 4.24 and 4.25).

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References

1 Joshi P C, Mandal S, Das P C & Chatterjee A, *Phytochemistry*, 28, **1989**, 1281.
2 Joshi P C, Mandal S, Das P C & Chatterjee A, *Phytochemistry*, 30, **1991**, 2094.
3 Joshi P C, Mandal S, Das P C & Chatterjee A, *Phytochemistry*, 32, **1993**, 481.
4 Reisch J, Szendrei K, Minver E & Novak I, *Experientia*, 24, **1968**, 992.
5 Banerji J, Ghosal N, Sarkar S & Kumar M, *Indian J Chem*, 21B, **1982**, 496.